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Reliability of portable X Rays Fluorescence for the chemical characterisation of ancient corroded copper-tin alloys

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Abstract

This paper examines the effect of different corrosion patinas on the chemical composition of coppertin alloys detected by portable X-ray Fluorescence Spectroscopy (pXRF). Specimens of Cu₈₈Sn₁₂ alloy with a composition close to that of ancient Egyptian copper-based alloys were corroded in three different aqueous solutions containing aggressive anions that can be found in Egyptian soil, for a maximum time of three months. After each sample was extracted, the elemental composition was determined with pXRF and the surface morphology and cross-sections were observed by metallographic microscopy to measure the thickness of the corrosion patinas. The cross-section of selected samples was analysed with Scanning Electron Microscopy equipped with Energy Dispersive X-ray Spectrometer (SEM-EDS). During the corrosion evolution of the copper alloy in the corrosive solutions of chlorides, decuprification phenomena made XRF data less accurate due to the development and thickening of Sn compounds (oxides or chlorides). Another problem encountered in the detection of the chemical composition of the Cu₈₈Sn₁₂ alloy was the bronze disease that strongly increased the corrosion process leading to the formation of an outer layer of atacamite and paratacamite, reaching a thickness of 150 µm. Conversely, during the corrosion process of the samples immersed in a sulphate solution, no changes in the initial composition of the Cu₈₈Sn₁₂ alloy were observed. The attenuation effect of the Sn concentration, by the thickness of green/dark green patinas with a high chloride content was observed on two Egyptian toilet spoons from the Museo Egizio (Turin) using pXRF. Following comparison of the chemical compositions in different corrosion patinas, it emerged that the red and grey patinas did not suffer the attenuation effects and, at these points of analysis, a reliable chemical characterisation of the alloy was obtained.

Keywords

Portable X-ray Fluorescence; Copper alloy; Corrosion; Bronze; ancient Egypt.

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